



## Leaching and homogeneous contribution in liquid phase reaction catalysed by solids: The case of triglycerides methanolysis using CaO

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### ABSTRACT

This work investigates two fundamental aspects faced in the heterogeneous catalytic reaction in liquid phase: leaching of species from the solid and the participation of these species in the catalytic reaction. Particularly we have focused on the transesterification of triglycerides with methanol catalysed by solid CaO to produce biodiesel. The first aspect affects the industrial application as extensive leaching may threaten the reusability and the environmental sustainability of catalyst. A method based on in situ conductivity measurements has been used to quantify the amount of solid that is solubilised. This in situ methodology is very helpful in the case of solids sensitive to CO<sub>2</sub> and H<sub>2</sub>O present in ambient atmosphere, as it is the case of CaO. The amount of CaO that can be solubilised in methanol, and for the first time, in glycerol–methanol and in biodiesel–glycerol–methanol mixtures has been investigated. Larger amount of leached species was observed when glycerol is present because Ca diglyceroxide is formed due to the reaction between CaO and glycerol and this is a more soluble compound than CaO. Notwithstanding this, the solid can be reutilised for a reasonably large number of runs under the catalyst loading frequently used (larger than 1 wt% referred to oil). The second investigated aspect refers whether the solid can be considered just a source of leached active homogeneous species. It was found that the homogeneous contribution arising from the leached species can be considered negligible provided that the catalyst loading is that often used (close to or larger than 1 wt% referred to oil). The methodology and principles used in this work may be also relevant to other heterogeneous reaction carried out in liquid phase.

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### 1. Introduction

The transesterification with methanol of the triglycerides present in the vegetable oils and animal fats results in the formation of a mixture of fatty acid methyl esters (FAME), also known as biodiesel [1–4]. A solid catalyst with high activity can get rid off the drawbacks of the homogeneous catalyst used in the industrial process: corrosiveness of the catalyst and the large amount of wastewater required for washing the products. The search has attracted the interest of many researchers [5]. CaO has been revealed as a very promising basic heterogeneous catalyst for the synthesis of biodiesel at mild temperatures (below the boiling point of methanol) and at atmospheric pressure [6–13]. However after numerous studies some important questions from the fundamental and applied point of view remain yet unclear. To our knowledge, there is no information concerning the leaching of CaO in the reaction medium.

The determination of the amount of CaO leached by dissolution of the solid in the reaction medium is relevant for the following reasons. First, leached species can show homogeneous catalytic activity whose contribution must be compared with that arising from sites at the surface of the solid (heterogeneous contribution). Second, the presence of Ca<sup>2+</sup> in the alcoholic phase and in the ester phase has implications in the water consumption for rinsing of the products, especially the biodiesel. Ca concentration in the biodiesel is limited by strict regulations. Finally the degree of leaching directly affects the number of runs that the catalyst can be reutilised when operating in batchwise mode or the time of operation when working in a continuous process.

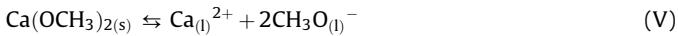
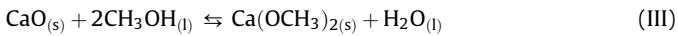
To estimate the homogeneous contribution of leached species requires first the determination of the amount of CaO solubilised in the reaction mixture. This quantification is not an easy task. Conventional separation techniques like filtration or centrifugation are not very suitable because they are usually carried out under ambient conditions. However data at higher temperature [40–60 °C] are required because methanolysis is usually performed at those temperatures and this complicates the experimental set-up for the determination of CaO solubility. Moreover the contact

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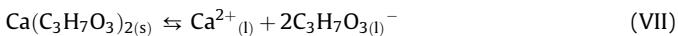
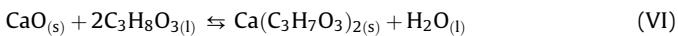
with room air must be prevented because the leached species can react with atmospheric  $\text{CO}_2$  resulting in the likely formation of  $\text{CaCO}_3$  that is insoluble. And finally filtration is normally driving by vacuum and the evaporation of methanol can result in an overestimation by concentration of the dissolved species.

It must be also taken into account that the dissolution process involves a complex network of reactions. First, the equilibrium of dissolution of  $\text{CaO}$  in methanol must be considered (reaction (I)). Second, the surface of  $\text{CaO}$  is unavoidable covered by  $\text{Ca(OH)}_2$  layers. Very low  $\text{H}_2\text{O}$  partial pressure ( $p \leq 5 \times 10^{-9}$  Torr) is required at room temperature to prevent the formation of surface  $\text{Ca(OH)}_2$  [7,14,15] because of the reaction of  $\text{H}_2\text{O}$  and the strong basic  $\text{O}^{2-}$  sites present at the surface of  $\text{CaO}$ . This extremely low partial pressure can only be reached under the extremely controlled atmosphere of UHV equipments. In practical terms and under conditions frequently faced in common equipments  $\text{Ca(OH)}_2$  is formed and then the reaction (II) must be also contemplated. Moreover  $\text{Ca}$  methoxide can be formed by the reaction of  $\text{CaO}$  and  $\text{Ca(OH)}_2$  with methanol as has been already reported by Kouzu et al. [11] and therefore the equilibrium of formation and dissolution of  $\text{Ca}$  methoxide in methanol must be also considered (reactions (III)–(V)):



The (s) and (l) subscripts refer to solid and liquid alcoholic phase, respectively. It is implicitly assumed that the dissolution process occurs only in the alcoholic phase and that the ester phase does not participate of the dissolution process. This approximation is based on the experimental data that have shown that any ionic species in the methanolysis reaction is basically concentrated in the alcoholic phase [3].

The situation is even more complex than that represented in reactions (I)–(V). The glycerol released during the transesterification reaction reacts with  $\text{CaO}$  forming  $\text{Ca}$  glyceroxides [11,16]. Therefore although the solid starts as  $\text{CaO}$  at the beginning of the reaction, various  $\text{Ca}$  glyceroxides can be formed as the transesterification reaction progresses. Consequently the dissolution of  $\text{Ca}$  glyceroxides summarised in the reactions (VI) and (VII) must be also considered. For the sake of simplicity only the case of  $\text{Ca}$  diglyceroxide from  $\text{CaO}$  is presented but similar reactions with  $\text{Ca(OH)}_2$  and with other glyceroxides can be contemplated:



In this work we present the investigations carried out to quantify the solubility of  $\text{CaO}$  not only in methanol but also in methanol–glycerol and methanol–glycerol–biodiesel mixtures. To our knowledge the latter two systems have never been investigated. The solubility of  $\text{CaO}$  in glycerol was not considered as such situation is never occurring during the progress of the reaction: as soon as glycerol is released  $\text{CaO}$  reacts and forms glyceroxides. Two different experimental methodologies have been used; *in situ* filtration with basket submerged in the liquid medium and the *in situ* measurements of conductivity of the liquid in contact with the solid. In basket method  $\text{Ca}^{2+}$  concentration is determined whereas with the conductivity approach the equivalent amount of  $\text{CaO}$  dissolved is determined. In a

second type of experiments, catalytic tests were also performed in order to estimate the contribution of the homogeneous leached basic species in comparison with that arising from the solid. The effect of free fatty acids (FFA) in the solubilising of  $\text{Ca}$  phases and in the leaching of species was not considered as this work deals with refined oils with very low FFA content.

## 2. Materials and experimental

### 2.1. Materials

The  $\text{CaO}$  that was used was freshly prepared for the different experiments by decomposition of  $\text{CaCO}_3$  precursor (Aldrich, ACC reagent) at 1073 K for 1 h under  $\text{O}_2/\text{Ar}$  atmosphere. This thermal treatment results in the total decarbonation of the precursor. The required amount of  $\text{CaCO}_3$  was sieved as to obtain particles between 0.42 and 0.5 mm and loaded in a quartz microreactor and then the temperature was raised up to 1073 K (heating rate 5 K min<sup>-1</sup>) while flowing 40 mL min<sup>-1</sup> (STP) of 20%  $\text{O}_2/\text{Ar}$ .  $\text{O}_2$  (>99.995%) and Ar (>99.999%) cylinders were supplied by Alphagaz. Once at room temperature the  $\text{CaO}$  so formed was transferred from the microreactor to the experimental set-up for the solubility measurements preventing the contact with the room atmosphere.

Methanol (Riedel de Haën, Reag. Ph. Eur., >99.8% GC,  $\text{H}_2\text{O} < 0.005\%$ ) and glycerol (Sigma, Reagent Plus, >99% GC) were used as received. The biodiesel used in this study was prepared by transesterification of sunflower oil (refined food grade) with methanol by using 1% KOH (Panreac, 90%) in methanol. The reaction conditions were: 333 K, methanol/oil molar ratio = 13, 1000 rpm, reaction time 4 h. The ester phase obtained was purified by washing first with hydrochloric acid 0.125 M in water and later with dichloromethane. Further purification was done by distillation in a rotary evaporator at 333 K and  $\approx 10$  kPa for 2 h. The content in fatty acid methyl ester was determined by GC (further details of the analysis was given elsewhere [7,17]) and found to be >96 wt%. The presence of FFA in this biodiesel must be negligible as they must be fully removed by reaction with the excess of KOH used during transesterification and by washing steps.

### 2.2. Determination of $\text{CaO}$ solubility by *in situ* filtration with a basket submerged in the liquid medium

A three-necked 125 mL glass jacketed reactor was used. A reflux condenser was connected to one of the necks, other neck was used for sampling by a syringe and the third one was used to hang a basket. The reactor was heated by a water recirculating bath. The basket was an *ad hoc* prepared cartridge made of stainless steel mesh (Goodfellow, AISI316, nominal aperture of the mesh 0.103 mm, wire diameter: 0.066 mm). Other commercial cartridges made of cellulose, glass or quartz could not be used because it was tested that basic species like  $\text{OH}^-$  or  $\text{CH}_3\text{O}^-$  in dissolution were neutralised because of the reaction with some reactive sites present in those cartridges.

The glass reactor was flushed with 50 mL min<sup>-1</sup> (STP) of Ar for 2 h as to remove any trace of room air. Then 33 mL of methanol was poured and heated up to 333 K. 100 mg of activated  $\text{CaO}$  particles (0.42–0.5 mm) were loaded in the basket preventing any contact with room air. The basket with the solid was then submerged in the methanol at 333 K while stirring at 300 rpm and the reactor was closed. Sampling of ca. 1 mL of methanol at different contact times was carried out. The syringe was previously loaded with ca. 1 mL of diluted HCl to prevent the formation of  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$ . This solution was transferred to a flask, the methanol removed by heating at 343 K for 1 h and the diluted HCl solution was added up to 10 mL of solution. The  $\text{Ca}^{2+}$  content of this solution was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-

AES) using a Perkin-Elmer Optima 3300 DV instrument. The CaO dissolved in methanol can then be estimated from the  $\text{Ca}^{2+}$  concentration detected in methanol.

### 2.3. Determination of CaO solubility by *in situ* conductivity measurements of the liquid in contact with the suspended solid

The experimental set-up used for the measurements of conductivity is similar to that of Section 2.2 but instead of the cartridge, a conductimeter (Crison Mod. Basic 30 with conductivity cell 5293) was placed in contact with the selected solution that contains a given amount of dispersed solid. The incorporation of the solid was done following similar procedures described in previous section. The conductivity was measured under strong agitation (1000 rpm) unless otherwise stated. First, it was measured at 333 K after a long equilibrium time (ca. 1000 min). Then the temperature was cooled down at 298 K and conductivity measured again after 2 h at this temperature. The conductivity of pure liquids was very low (few  $\mu\text{s cm}^{-1}$ ) and always subtracted from the values of the solid–liquid mixtures.

The procedure to determine the solubility is based on the following considerations. When very little amount of activated CaO was added to an alcoholic medium it will be fully dissolved. The conductivity of the solution will be the result of the ionic species described in equilibria of reactions (I)–(VII). When the amount of added CaO is larger than the quantity that can be dissolved, then further addition of solid will not result in an increase of the conductivity. This threshold is governed by the equilibrium constants of reactions (I)–(VII). In a figure representing the conductivity vs. the amount of CaO added there will be two regions; first region is beyond the CaO solubility value in which the conductivity will be constant irrespective the amount of solid added to the liquid. In the other region which is below the CaO solubility value the CaO will be fully solubilised and the conductivity decreases upon decreasing the CaO addition. The solubility of CaO can be obtained by the crossing of the extrapolation of both trends.

The conductivity measurements in pure methanol were done by adding CaO to ca. 70 mL of the alcohol. In the case of glycerol–methanol mixtures, CaO was added to a mixture of glycerol and methanol with a volumetric ratio = 1:4. This mixture corresponds to a methanolysis reaction carried out with an oil/methanol ratio = 10 and assuming total conversion. This ratio is close to that frequently found in the methanolysis of triglycerides reported in commercial applications and research works [1,2,5–13]. In the case of biodiesel–glycerol–methanol mixtures, 50 mL of biodiesel were added to the 18 mL of glycerol and 72 mL of methanol. It must be said that this volumetric ratio cannot be obtained from an initial mixture of methanol/oil with vol. ratio = 10. In this case there is an excess of biodiesel, but this fact does not affect the conclusions as the goal is to saturate the alcohol phase with biodiesel. In this case the experiments were conducted as follows: CaO and the liquids were subjected to a strong agitation at 1000 rpm for 30–60 min in order to accelerate the building up of the equilibrium concentration of alcohols within the biodiesel phase and vice versa. Then the agitation was lowered down to 300 rpm and two phases separate: the ester phase (upper) and the alcoholic phase (lower). Under this smoother agitation the solid is suspended in the lower (alcoholic) phase. The conductivity of the alcoholic phase with the solid suspended in it was then measured. If faster stirring was used then the conductivity value would be perturbed by the presence of biodiesel drops within the conductivity cell.

### 2.4. Catalytic activity measurements

The catalytic reaction was carried out in a three-necked jacketed batch reactor. A reflux condenser was connected to one

of the necks, another neck was for introducing the thermocouple and the tubing for  $\text{N}_2$  flow and a dropping funnel was connected to the third one for oil addition. The dropping funnel was replaced by a syringe for sampling from the reaction mixture once the oil was added. The reactor was flushed with  $\text{N}_2$  (50  $\text{mL min}^{-1}$ ) for more than two hours in order to remove any trace of room air. A selected amount of CaO prepared as described in Section 2.1 was added to a given alcoholic mixture in the reactor and set at 333 K, and afterwards 50 g of oil (refined sunflower oil, food grade) was added ( $t = 0$  min. of the reaction). The reaction mixture was maintained under static  $\text{N}_2$  and under vigorous agitation (1000 rpm) while performing the catalytic reaction.

Two different amounts of CaO were utilised. In order to assess on the intrinsic activity of the homogeneous species very little amount of CaO was added as to be fully solubilised in the alcohol medium. In a second type of experiment a larger amount of CaO was added as to have both leached species and solid catalyst, the catalytic reaction arises from the leached species and from the active sites at the surface of the solid (heterogeneous reaction). Once the reaction has started aliquots (ca. 2 mL) were taken from the agitating reaction mixtures at different reaction times. The reaction was quenched by addition of the aliquots to an aqueous HCl solution. The content in FAME of the organic layer after several washing steps was determined by following the European regulated procedure EN 14103. Further details of the washing steps and of the analytical procedure can be found elsewhere [7].

## 3. Results and discussion

### 3.1. Solubility of Ca in alcoholic mixtures

#### 3.1.1. Solubility of CaO in methanol

The solubility of CaO in methanol was determined by the two methods: the *in situ* filtration and the *in situ* conductivity measurements. After 1 h of contact 0.134 mg of CaO was dissolved per mL of methanol. The amount of CaO solubilised in methanol increases as the CaO stays submerged for longer periods. After 3 h of immersion 0.169 mg of  $\text{CaO mL}^{-1}$  was dissolved in methanol and after 6 h apparently the solubility was 0.532 mg  $\text{CaO mL}^{-1}$  of methanol.

Fig. 1A represents the conductivity ( $\kappa$ ) of CaO–methanol mixture vs. the amount of solid CaO added per mL of methanol at 333 and 298 K. Fig. 1B shows the variation of the conductivity with time of contact at 333 K for the case of 0.6 mg of solid  $\text{CaO mL}^{-1}$  of methanol. Similar trends were observed for the rest of conductivity measurements at 333 K. The conductivity value goes through a maximum that can be explained considering that several process are involved: the rising of temperature up to 333 K, the kinetics of dissolution and the exothermic character of the dissolution process then (solubility decreases as temperature increases). The value after 1000 min at 333 K is selected but it can be observed that as soon as the temperature is equilibrated at 333 K the conductivity has almost reached the steady state value (at 100 min. the system reached a value for the conductivity very close to that after 1000 min). Then the temperature was cooled down to 298 K. The steady state value is rapidly reached (in few minutes) but for the sake of accuracy the value after 2 h was recorded.

Fig. 1A clearly shows that, irrespective the temperature, the conductivity initially rises upon increasing the amount of CaO in methanol. After a certain value of CaO concentration the conductivity remains constant. The extrapolation of both trends results in a crossing point that gives an estimation of the maximum amount of CaO that can be dissolved in methanol. Two lines have been drawn to estimate the crossing point. It must be clearly stated that the line representing the behaviour at low CaO loading is just a visual guide as the conductivity dependence at this low

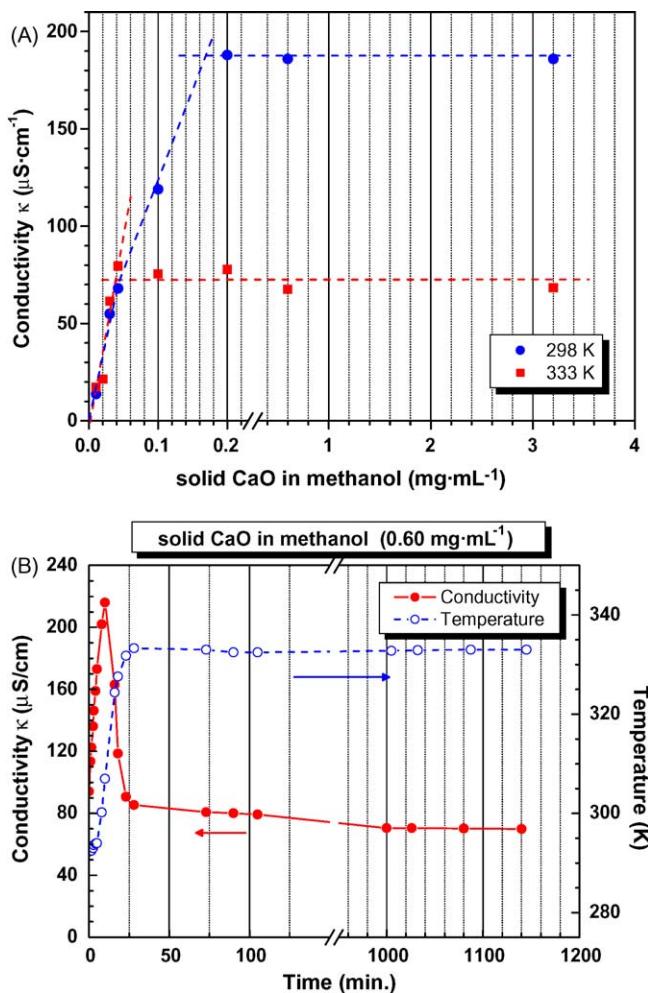


Fig. 1. (A) Conductivity at 298 and 333 K of  $\text{CaO}$ -methanol mixtures vs. the initial amount of  $\text{CaO}$  loaded per mL of methanol. (B) Conductivity vs. time dependence obtained with  $0.6 \text{ mg of CaO mL}^{-1}$  of methanol at 333 K.

concentration is expected to be more complex than that drawn. It is clear that at 333 K the solubility of  $\text{CaO}$  is between 0.03 and  $0.04 \text{ mg of CaO mL}^{-1}$  of methanol. At 298 K the solubility is between  $0.1$  and  $0.2 \text{ mg of CaO mL}^{-1}$ , a larger value than that obtained at 333 K. The dissolution process of  $\text{CaO}$  in methanol is exothermic (an increase of the temperature of methanol was observed when  $\text{CaO}$  was added at room temperature), so a decrease of the temperature must result in a shift of the equilibrium towards an increase of the solubilisation.

The value at 333 K,  $0.04 \text{ mg of CaO mL}^{-1}$ , can be compared to those obtained from in situ basket methodology. After 1 h of contact time the Ca concentration in methanol measured by in situ filtration was  $0.134 \text{ mg of Ca mL}^{-1}$ . This value is more than three times larger than that determined in Fig. 1A. The differences are even larger at longer contact time of immersion (ca. 4 and 13 times larger for 3 and 6 h of contact time). Since the differences cannot be attributed either to mass transfer restrictions to the dissolution process or to the lack of achievement of the equilibrium in the conductivity measurements (strong agitation for ca. 1000 min was used), it can be concluded that the in situ filtration leads to overestimated values. Although smooth agitation was used in the basket method, it was observed that the deficient mechanical properties and fragility of  $\text{CaO}$  particles results in breaking up into particles finer than the nominal aperture of the mesh of the basket ( $<0.103 \text{ mm}$ ). Very fine particles, not retained in the basket,

detectable by visual inspection, end up in the methanol. This interferes with the determination of solubility of  $\text{CaO}$  and results in an overestimation of the concentration of Ca in methanol. We believe that the basket methodology must be discarded because although finer mesh can be used, there will be always doubts about the consistency of the measurements with basket. Particles finer than the aperture of the mesh can always be formed and mass transfer restrictions to the free exchange of alcohol and ions between the inner liquid region and the outer liquid region of the basket can also be expected. In conclusion conductivity methodology appears as a more reliable methodology to measure the solubility of  $\text{CaO}$  in methanol.

According to the conductivity methodology, less than  $0.04 \text{ mg of CaO mL}^{-1}$  are solubilised in methanol at 333 K, a very representative temperature of reaction. Expressed as  $\text{Ca}^{2+}$  concentration, it is equivalent to  $0.028 \text{ mg of Ca mL}^{-1}$  of methanol. This cation concentration is much smaller than that found in the case of homogeneous catalyst. In a typical transesterification reaction carried out by 1 wt%  $\text{NaOH}$  (with respect with oil) and by using the very common oil/methanol molar ratio = 6, the concentration of Na in methanol will be ca.  $21 \text{ mg Na}^+ \text{ mL}^{-1}$ , that is 750 times larger than that of  $\text{Ca}^{2+}$ . This estimation gives an idea how small the concentration of leached ionic species must be at the beginning of the reaction catalysed by  $\text{CaO}$  in comparison with that found in the reaction carried out with a homogeneous catalyst.

Apparently the leaching of basic species by dissolution of the  $\text{CaO}$  in the alcohol medium is quite small. However it must be taken into account that as the transesterification reaction progresses, glycerol is released that reacts with  $\text{CaO}$  forming  $\text{Ca}$  glyceroxides [11,16]. Therefore a study of the solubility of  $\text{CaO}$  in glycerol–methanol mixture is required.

### 3.1.2. Solubility of $\text{CaO}$ in biodiesel–glycerol–methanol and in glycerol–methanol mixtures

The solubility of  $\text{CaO}$  in biodiesel–glycerol–methanol mixture (v/v ratio 50:18:72) was also recorded. The results are represented in Fig. 2, the concentration is presented as solid  $\text{CaO}$  added per mL of alcoholic mixture. It can be concluded that at 333 K the amount of  $\text{CaO}$  beyond which the conductivity is constant is very close to  $0.6 \text{ mg of CaO mL}^{-1}$  of alcohol. When more than  $0.6 \text{ mg of CaO}$  is added per 1 mL of alcoholic mixture, not all the solid is solubilised as some turbidity was clearly observed. The conductivity does not rise above this value. Below this amount the solid was fully

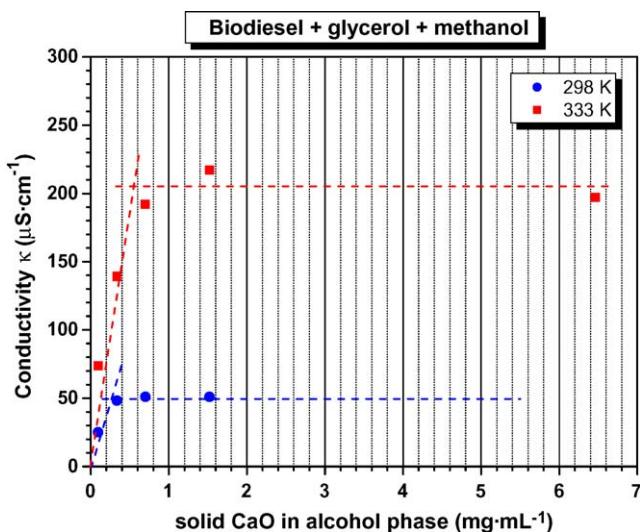


Fig. 2. Conductivity at 298 and 333 K of  $\text{CaO}$ -biodiesel-glycerol-methanol mixtures vs. the initial amount of  $\text{CaO}$  loaded per mL of alcoholic phase.

dissolved and no solid suspended in the liquid was detected by careful visual inspection. Then the conductivity decreases upon diminishing the amount of CaO in the mixture. Very recently Kouzu et al. [18] reported an investigation on the leaching of CaO in the alcohol phase after conducting the methanolysis of triglycerides under condition very similar to those used by us except that the catalyst loading was larger (0.8 wt%) and the reaction temperature was higher (refluxing methanol). They found that only a little fraction is dissolved in the biodiesel phase and that after the first run the  $\text{Ca}^{2+}$  concentration in pure glycerol was 4602 ppm. This corresponds to ca. 1 mg of equivalent CaO per mL of final alcoholic phase (methanol and glycerol). The latter value compares reasonably well with our data which is ca. 0.6 mg of equivalent CaO  $\text{mL}^{-1}$  of alcohol (methanol and glycerol) if we take into account that we measured the solubility at different temperature (333 K) and with a different methodology. At 298 K the solubility of CaO is clearly smaller: less than 0.4 mg of CaO  $\text{mL}^{-1}$  of alcohol. It seems very reasonable to propose that the solubilisation of the Ca diglyceroxide in biodiesel–glycerol–methanol mixtures is not an exothermic process, as the solubility does not decrease with the temperature, in contrast to the case of CaO in methanol that is exothermic.

The solubility of CaO in glycerol–methanol mixtures was also investigated following the same conditions as above except that biodiesel was not added. The solubility was then found to be slightly larger than that found in biodiesel–glycerol–methanol mixtures (ca. 1 mg of solid CaO  $\text{mL}^{-1}$  of alcohol). It seems that the presence of biodiesel slightly reduces the solubility of CaO in glycerol–methanol mixtures.

If we consider that CaO solubility in biodiesel–glycerol–methanol mixtures at 333 K is 0.6 mg of equivalent CaO  $\text{mL}^{-1}$  of alcohol solution that means that the  $\text{Ca}^{2+}$  concentration in the final alcoholic mixture is 0.42 mg of  $\text{Ca}^{2+}$   $\text{mL}^{-1}$ . The metal concentration in the alcoholic mixture is still much lower than that found when the reaction is catalysed by homogeneous catalysts. Thus if we use 1 wt% of NaOH the  $\text{Ca}^{2+}$  concentration is 50 times lower than that of  $\text{Na}^+$  (21 mg of  $\text{Na}^+$   $\text{mL}^{-1}$ ). This has implications in the purification process of the raw biodiesel and of the glycerol obtained in the transesterification reaction catalysed by CaO because less demanding washing procedures is required. It must be also stressed that the  $\text{Ca}^{2+}$  concentration in the reaction mixture must be constant disregarding the initial CaO loading as it arises from the solubility of the Ca diglyceroxide phase. Therefore a CaO loading larger than that frequently used for NaOH or KOH (1 wt% referred to oil) can be used without increasing the  $\text{Ca}^{2+}$  concentration in the reaction mixture.

### 3.2. Transformation of CaO during the progress of the reaction

In an attempt to see, as suggested above, whether CaO is being transformed to other compounds because of the reaction with methanol and/or with glycerol, the following experiments were conducted. First ca. 300 mg were added to ca. 30 mL of methanol and set aside for several days at room temperature. Then XRD pattern of the powder is represented in Fig. 3A that shows that the pattern is similar to that reported by Kouzu et al. [11] and that was assigned by them to  $\text{Ca}(\text{OCH}_3)_2$  (Ca methoxide). Most of the peaks can be assigned to the JCPDS file 31-1574 of Ca methoxide (marked as ■). The peak at  $2\Theta = 30.3^\circ$  (▼) appears indexed in another JCPDS file 20-1565 as arising also from Ca methoxide along with other reflections coincident with those of JCPDS file 31-1574. The peak at ca.  $2\Theta = 40.4^\circ$  remains unassigned but it does not arise from either CaO, or  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$ . It seems that a correct elucidation and indexation of the XRD of Ca methoxide reflections is still required because two different Ca methoxide crystal structure

may exist. However it is very reasonable to propose that as CaO reacts with methanol,  $\text{Ca}(\text{OCH}_3)_2$  is formed at the expenses of CaO. Fig. 3B shows the XRD pattern obtained when CaO contacted a biodiesel–glycerol–methanol mixture. In this case ca. 585 mg of CaO were added to the biodiesel–glycerol–methanol mixture and after the conductivity at 333 K was measured, then it was cooled down to room temperature (it corresponds to the experiments with 6.5 mg of CaO  $\text{mL}^{-1}$  of Fig. 3). The solid was recovered by filtration, washed with methanol and rapidly collected and stored under  $\text{N}_2$  until the XRD pattern was recorded. Fig. 3B shows the diffractogram of this solid. The pattern coincides peak by peak (■) with those assigned by Kouzu et al. [11] to Ca diglyceroxide,  $\text{Ca}(\text{C}_3\text{H}_5\text{O}_3)_2$ . They demonstrated that when CaO is in contact with glycerol–methanol mixture a solid appeared that they have assigned to Ca diglyceroxide. They also demonstrated by XRD, IR and  $^{13}\text{C}$  NMR characterisation that when they carried out the methanolysis of oil by using solid CaO, the final solid recovered once the reaction has proceeded up to large conversion to FAME is not CaO but also Ca diglyceroxide. No reflections could be assigned to CaO,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OCH}_3)_2$  nor to any of the other Ca glyceroxides that have been described (Ca monoglyceride, Ca octaglyceride and Ca hexaglyceride) [16]. For the sake of simplicity we still keep the measurement of solubility as mg of equivalent CaO although this solid is not present in any of the final mixtures.

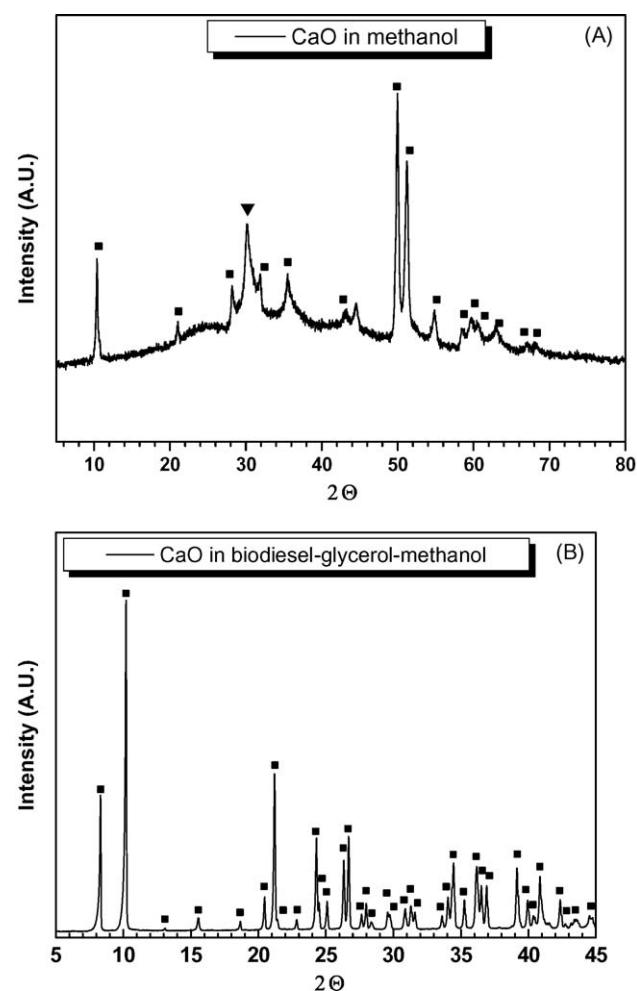


Fig. 3. XRD patterns of the solids obtained after contacting CaO (A) with methanol and (B) with biodiesel–glycerol–methanol mixtures.

Another interesting comment worthy to stress is that, from the data presented above in Fig. 3 and from those reported elsewhere [11,19], it can be deduced that during the first moments of the reaction when CaO contacts methanol,  $\text{Ca}(\text{OCH}_3)_2$  is formed at the expenses of CaO. As the reaction progresses glycerol is formed that reacts with the  $\text{Ca}(\text{OCH}_3)_2$ ,  $\text{Ca}(\text{OH})_2$  or CaO forming Ca diglyceroxide. Both Ca methoxide and Ca diglyceroxide has been showed to be active in the triglycerides methanolysis. Once the reaction has been completed the only phase observed in the recovered solid is Ca diglyceroxide. That means that if we use the latter solid in successive runs we are not dealing anymore with CaO but with Ca diglyceroxide. The solubility of CaO in biodiesel–glycerol–methanol mixtures is then primarily defined by the solubility of the diglyceroxide.

The solubility of Ca diglyceroxide in methanol has been reported to be 1.2 mg of equivalent  $\text{CaO mL}^{-1}$  of methanol at 298 K [16]. The latter data are in the same range to those found in this article for the solubility of Ca diglyceroxide at 333 K in glycerol–methanol (1 mg of equivalent  $\text{CaO mL}^{-1}$ ) and biodiesel–glycerol–methanol (0.6 mg of equivalent  $\text{CaO mL}^{-1}$ ).

An estimation of the number of reaction runs that the CaO initially loaded can be reused until full dissolution can be done from the data of Figs. 1 and 2. If one considers that the dissolved CaO arises from the dissolution of Ca diglyceroxide in biodiesel–glycerol–methanol mixtures (the final mixture achieved when the reaction is completed) and if one assumes that the solubility at 333 K is that deduced from Fig. 2, then around 0.6 mg of equivalent  $\text{CaO mL}^{-1}$  of alcoholic mixture is dissolved in every run. Under typical reaction conditions like 1% of catalyst loading (with respect to oil) and methanol/oil molar ratio of 6, the initially loaded CaO will be fully dissolved in around 75 runs. This latter value is much smaller than that estimated if we consider that Ca diglyceroxide was not formed and the only source of dissolution is that of CaO in methanol which according to Fig. 1 is 0.04 mg  $\text{CaO mL}^{-1}$  of methanol (then the numbers of run would be ca. 1130 runs). Therefore, the fact that Ca diglyceroxide is formed and that this is more soluble in the biodiesel–glycerol–methanol mixtures than Ca methoxide is in methanol considerably reduces the expectations in the number of reutilisation runs. In any case the CaO can be still reutilised a quite large number of runs provided that the catalyst loading is that frequently used (1 wt% or even larger). It must be reminded that using initial CaO loading much larger than 1 wt% will remarkably increase the reaction rate without increasing the  $\text{Ca}^{2+}$  concentration in the reaction mixture as this is defined by the solubility constant. The number of reutilisations above calculated is just estimation because the data of solubility were obtained when a steady value of conductivity was achieved and because of the presence of FFA that react and dissolve Ca phase was not contemplated. But the conclusions are still valid. The estimated number of runs that CaO can be reutilised is in agreement with those found in other reports [12,20] in which the CaO catalyst was recycled for a large number of runs (20 runs) without significant decay of the conversion as loading larger than 1 wt% was used. If the catalyst loading is smaller than 1 wt% then the number of reutilisation cycles is smaller as it has been recently confirmed [21].

### 3.3. Heterogeneous contribution vs. homogeneous contribution

In principle there can be two pathways for conversion: that involving the surface sites of the solid (heterogeneous mechanism) and that involving the leached species by dissolution of the solids in the reaction medium (homogeneous mechanism). In a previous work it was clearly shown that both mechanisms can be contributing to the transformation of triglycerides to FAME. However a reliable determination of their share to the total

conversion could not be accomplished at that time because of the uncertainty derived for the method utilised in that work [7]. When considering this question in a batch discontinuous operation, it must be borne in mind that (i) during the first run the initially loaded CaO is gradually transformed to Ca diglyceroxide as the reaction progresses and glycerol is being released, then the species that are solubilised are changing with the progress of the reaction; (ii) at the end of the first run CaO has been fully transformed in Ca diglyceroxide and therefore in successive runs the latter solid is that initially present in the mixture; (iii) as the reaction progresses the alcoholic phase is changing from only methanol to glycerol–methanol mixtures, then the solubility of Ca diglyceroxide is changing and so does the contribution of leached species. Therefore the estimation of the contribution of homogeneous pathway is complicated because we are dealing with a very complex system and the composition of the alcoholic mixture and the solubility properties are changing.

In an attempt to estimate the homogeneous contribution in batch mode reaction we have considered two simpler experimental situations: a first one at the very beginning of the 1st run in which only CaO is present in the reaction medium (oil and methanol); and a second situation at the end of any run in which Ca diglyceroxide is present in an alcoholic medium that contains biodiesel, glycerol and methanol. A third situation which is Ca diglyceroxide mixed with only methanol, that occurring at the beginning of second and successive runs, is complicated to be experimentally determined because it will eventually evolve to that defined in the second point as glycerol is being formed. Moreover it must be reminded that the solubility of Ca diglyceroxide in methanol is of the same order in glycerol–methanol and biodiesel–glycerol–methanol mixtures and can be estimated from the second type of experiments.

Fig. 4 shows the progress of the reaction when two different samples of CaO were immersed in methanol: (3.3 and 0.134 mg  $\text{CaO mL}^{-1}$  of methanol). This is equivalent to the addition of 100 and 4 mg to reaction mixture, respectively. The reaction conditions were similar in the two cases (50 g of oil, 30 mL of methanol, methanol/oil molar ratio ca. 13, 333 K, 1000 rpm). In the latter case the FFA content in oil was previously removed by neutralisation to prevent the consumption of the catalyst. The experiments were carried out with 0.134 mg of  $\text{CaO mL}^{-1}$  of methanol representing a loading of CaO more than three times larger than that defined by the solubility of CaO in methanol, which

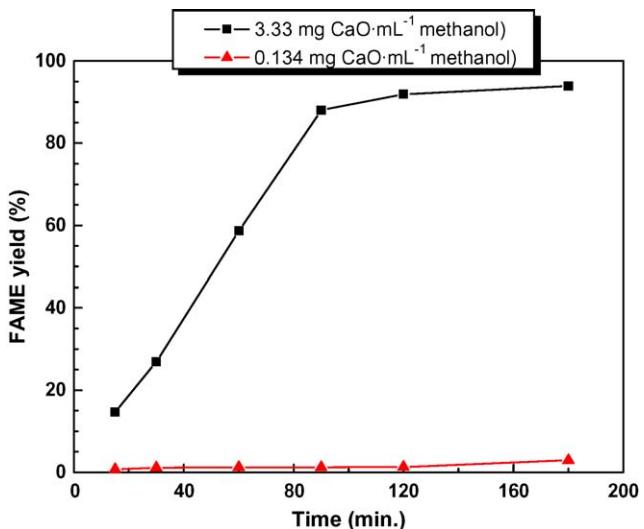
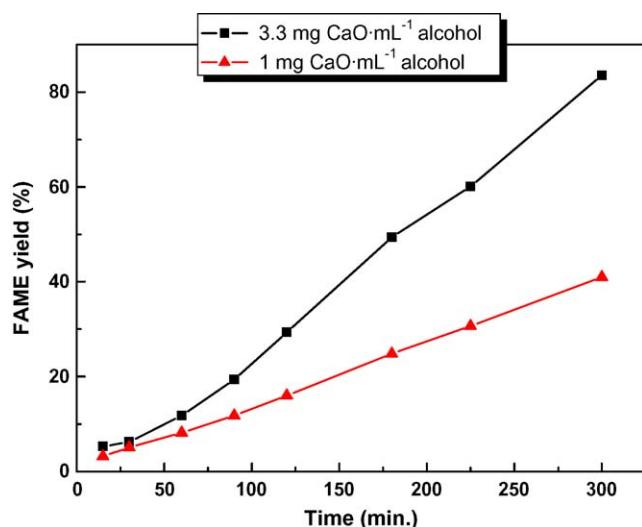


Fig. 4. FAME yield obtained with 4 mg and 100 mg of CaO. The reaction conditions were similar in the two cases (50 g of oil, 30 mL of methanol, methanol/oil molar ratio ca. 13, 333 K, 1000 rpm).



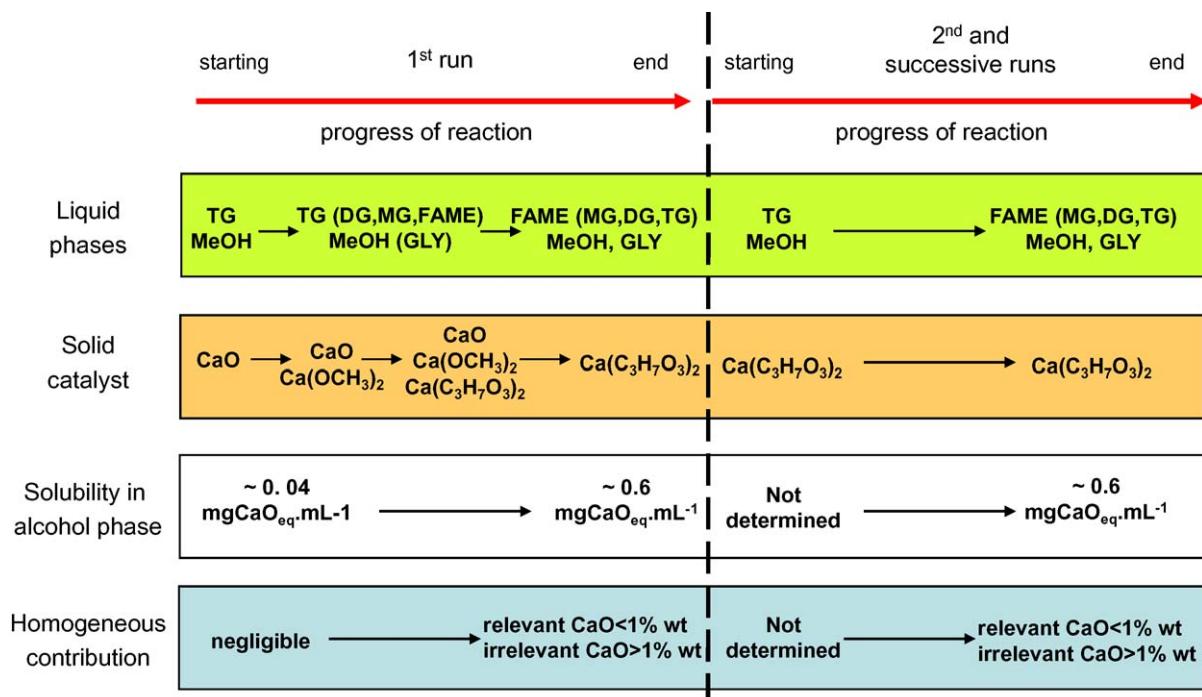
**Fig. 5.** FAME yield obtained when, before oil addition, 30 mg and 100 mg of CaO were contacted overnight with 30 mL of glycerol–methanol mixture ( $v/v = 0.25$ ) at 333 K to produce Ca diglyceroxide. The reaction conditions were similar in the two cases (50 g of oil, 30 mL of alcohol, alcohol/oil molar ratio ca. 13, 333 K, 1000 rpm).

is 0.04 mg of  $\text{CaO mL}^{-1}$ . Therefore in this case there is enough amount of CaO to have, besides leached species, a certain amount of solid particles in the reaction mixture (0.09 mg of  $\text{CaO mL}^{-1}$  of methanol). It can be clearly seen that the FAME yield obtained with the 0.134 mg of equivalent  $\text{CaO mL}^{-1}$  of methanol is remarkably much smaller than that obtained when 3.3 mg of equivalent  $\text{CaO mL}^{-1}$  of methanol. This indicates that the contribution of the homogeneous species created by leaching is negligible in comparison with that from the species at the surface of the solid.

Fig. 5 shows the FAME yield obtained when two different amounts of Ca diglyceroxide were used to carry out the transesterification reaction with a glycerol–methanol mixture.

This experiment provides information of the kinetics of the situation found at the end of every reaction run when working in batchwise operation. However considering that the solubility of Ca diglyceroxide in methanol is of the same order to that found in glycerol–methanol and biodiesel–glycerol–methanol mixtures (around 1 mg of equivalent  $\text{CaO mL}^{-1}$ ) this experiment can be also informative of the kinetics at the beginning of second and successive runs. Faster kinetics both in the homogeneous and in the heterogeneous pathways are expected in the latter case because of the absence of glycerol but the relative differences are supposed to be similar. To obtain the diglyceroxide, different amounts of CaO (30 and 100 mg) were contacted with 30 mL of a glycerol–methanol mixture ( $v/v = 0.25$ ) at 333 K overnight. They are equivalent to 1 mg and 3.33 mg of  $\text{CaO mL}^{-1}$  of alcohol mixture, respectively. Then 50 g of sunflower oil is added to this alcohol mixture and the reaction starts. In the case of the addition of 1 mg of equivalent  $\text{CaO mL}^{-1}$  of alcohol mixture, before the oil addition the initial mixture was clear transparent and no solid was observed by visual inspection. This is because this amount is close to the solubility of Ca diglyceroxide (expressed as mg of equivalent CaO) in glycerol–methanol mixtures. In Fig. 5 it can be clearly seen that the catalytic activity at this CaO loading is only slightly smaller than that found when 3.33 mg of equivalent  $\text{CaO mL}^{-1}$  of alcoholic mixture was used. Thus at 60 min, the FAME yield at lower catalyst loading is 8.2% and at larger loading is 11.7%.

A very interesting comparison rises when the initial intrinsic reaction rate is deduced from Fig. 5. This evaluation can give us a rough assessment of the intrinsic kinetics of the homogeneous and of the heterogeneous reaction at the end of any run. The initial intrinsic reaction was calculated from the conversion at 60 min, as at larger reaction time the conversion is larger than 10% and then the integral reaction rate may be obtained. On the other hand conversion at lower reaction time can result in larger uncertainty in the value. If we take into account that of the total conversion at 60 min with 100 mg of catalyst (11.7%), part is due to the 30 mg of Ca diglyceroxide which is dissolved (8.2%) and the rest (3.5%) is due to the 70 mg that remains undissolved (heterogeneous contribu-



**Scheme 1.** Liquid phases, solid catalyst transformation, solubility of the solids in the alcohol phase and homogeneous contribution during the progress of transesterification at 333 K reaction proposed in this article. The components between brackets are minor. (MG, DG and TG: mono-, di- and triglycerides; FAME: fatty acid methyl ester; GLY: glycerol; MeOH: methanol).

tion), then intrinsic activity of the homogeneous species must be close to  $7.2 \text{ mmol min}^{-1} \text{ mol}_{\text{eq,CaO}}^{-1}$  and that from the heterogeneous sites must be close  $1.4 \text{ mmol min}^{-1} \text{ mol}_{\text{eq,CaO}}^{-1}$ . Therefore the intrinsic kinetic of the homogeneous species is ca. five times faster than that of the active sites at the surface of the solid.

If so, apparently the homogeneous contribution must be quite important in comparison with that from the heterogeneous species. However the comparison between the activity of the homogeneous and heterogeneous species must also consider the total amount of the initially loaded CaO. We must bear in mind that 100 mg of CaO initially loaded represents 0.2 wt% of catalyst referred to oil weight, a very low catalyst loading when compared with those frequently used, very often larger than 1 wt%. Therefore in the latter cases the contribution from heterogeneous species at the surface of the solids must prevail over the homogeneous contribution.

Considering all the data presented in this work, the complex system under batchwise operation can be simplified as follows, see **Scheme 1**. This scheme specifically refers to the situation at 333 K but the conclusions can be extended to lower temperatures. CaO is the solid initially present in the oil–alcohol mixture at the beginning of the first run. CaO reacts with methanol and  $\text{Ca}(\text{OCH}_3)_2$  is progressively formed, this is the solid catalytically active during the starting of the reaction. At this point the reaction takes place predominantly at the surface of this solid and it is basically a heterogeneous driven reaction. The amount of solid that is solubilised in methanol is very small. As the reaction progresses and glycerol is released, Ca diglyceroxide is formed at the expenses of Ca methoxide. At the end of the run Ca diglyceroxide is present in the biodiesel–glycerol mixture. This solid is more soluble in the glycerol–methanol mixture than  $\text{Ca}(\text{OCH}_3)_2$  or CaO are in methanol. A first consequence of this fact is that the number of runs that the solid can be reutilised is much lower than that expected considering the very limited solubility of CaO in methanol, but still a large number if the initial catalyst loading is of the order of 1 wt% or larger. A second consequence is that the contribution of the solubilised species to the global reaction (homogeneous contribution) can become also more important than expected. If the amount of solid left at the end of any run is close to or larger than 1 wt% of equivalent CaO, then the heterogeneous contribution prevails at the end of the run. But if the amount of solid left at the end of the run is lower, the homogeneous contribution can be of the same order or even larger than that arising from heterogeneous centres. Kouzu et al. have proposed a mechanism for the methanolysis of triglycerides on Ca diglyceroxide [11].

The conclusions here presented are in harmony with the data very recently reported by Kouzu et al. [18]. They have investigated not only the first reutilisation cycle but also the second and successive runs (until four). Their result for the first reutilisation is in agreement with our result. However it must be stressed that they found that the extension of the leaching in the second and successive runs decreases and the  $\text{Ca}^{2+}$  concentration in the alcohol phase is half that found in the first cycle. Moreover they also observed that the soluble species in the second and successive runs are not active. More research is required to clarify these aspects.

Similar situations are expected in the case of continuous operation. A certain period of time is required to the system to reach a pseudo steady state defined by the extension of the transesterification reaction. The solid will be also transformed to Ca diglyceroxide and this phase will define the behaviour under similar considerations exposed in the later paragraph. Under continuous operation the conversion will decline with time as the Ca diglyceroxide is being removed from the reaction medium solubilised in the alcohol phase.

#### 4. Conclusions

Two fundamental aspects of the methanolysis of triglycerides to produce biodiesel by using CaO as heterogeneous catalysts have been investigated. The first aspect is the leaching of active species to the reaction mixture. The in situ conductivity measurements showed that the solubility of CaO in methanol was one order of magnitude smaller than that found in glycerol–methanol and in biodiesel–glycerol–methanol mixtures. In the latter cases ca. 1 mg and 0.6 mg of  $\text{CaO}_{\text{eq}} \text{ mL}^{-1}$  were solubilised, respectively, in the alcohol mixture at 333 K. The larger solubility in glycerol containing mixtures is due to the formation of Ca diglyceroxide that is more soluble in these mixtures than CaO is in methanol. In any case under frequent reaction conditions the  $\text{Ca}^{2+}$  concentration in glycerol containing mixtures and FAME phase is significantly lower than the metal concentration found when a homogeneous catalyst is used. Moreover the solid CaO can be reutilised for a reasonably large number of runs under catalyst loading larger than 1 wt% referred to oil.

The second fundamental aspect investigated was whether the leached species were active and whether the activity was comparable or not to that displayed by the active sites at the surface of the solid. The research allowed us to conclude that, although the intrinsic activity of the leached species was larger than that of the sites of the surface, the total homogeneous contribution is much smaller than that arising from the heterogeneous sites provided that the catalyst loading is larger than 1 wt% of CaO.

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